

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66647 A1

(51) International Patent Classification⁷: C09B 47/26.
C09D 11/00

(21) International Application Number: PCT/GB01/00565

(22) International Filing Date: 12 February 2001 (12.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0005301.7 7 March 2000 (07.03.2000) GB

(71) Applicant (*for all designated States except US*): **AVECIA LIMITED** [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PATEL, Prakash** [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). **WIGHT, Paul** [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).

(74) Agents: **MAYALL, John et al.**: Avecia Limited, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOUND, COMPOSITION AND USE

(57) Abstract: A compound of formula (1): $\text{Pc-SO}_2\text{-NH-CH}_2\text{CH}_2\text{-NH-CH}_2\text{CH}_2\text{NH-SO}_2\text{-Pc}$ wherein each Pc is independently an optionally substituted phthalocyanine groups provided that at most one of the groups represented by Pc carries a substituent of formula SO_2NH_2 . Also claimed are inks comprising these compounds, ink jet printer cartridges containing these inks, their use in ink jet printing and substrates printed with these compounds and/or inks.



WO 01/66647 A1

COMPOUND, COMPOSITION AND USE

This invention relates to dyes, to compositions containing these dyes, to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

5 There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water light and ozone fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink-jet nozzle because this will stop the printer from working. The inks should
10 also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

Dyes containing a single copper phthalocyanine group and their use in ink-jet printing are known. For example, C.I. Direct Blue 199 and C.I. Direct Blue 86 are used as colorants in commercial ink-jet printing inks. However, there is a continuing need to
15 provide colorants having superior properties in ink-jet printing inks.

According to the present invention there is provided a compound of Formula (1):



20 Formula (1)

wherein each Pc is independently an optionally substituted phthalocyanine group, provided that at most one of the groups represented by Pc carries a substituent of formula $\text{-SO}_2\text{NH}_2$.

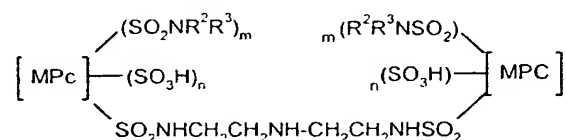
25 Preferred phthalocyanine groups represented by Pc are each independently selected from metal-free phthalocyanines and metal-containing phthalocyanines. More preferably phthalocyanine groups represented by Pc are each independently selected from copper phthalocyanine and nickel phthalocyanine.

The phthalocyanine group may contain further substituents. It is preferred that at
30 least one, and preferably both, of the phthalocyanine groups carries a sulpho substituent. It is also preferred that at least one and preferably both, of the phthalocyanine groups carries a sulphonamide substituent, preferably of the formula $\text{SO}_2\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are each independently H or optionally substituted alkyl, preferably H or optionally substituted C_{1-4} -alkyl, especially H or methyl, provided that at most one of the groups
35 represented by Pc carries a substituent of formula $\text{-SO}_2\text{NH}_2$. It is especially preferred that at least one of the phthalocyanine groups carries a sulpho substituent and a

sulphonamide substituent of the formula $\text{SO}_2\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are as hereinbefore defined.

The optional substituents which may be present on R^2 and R^3 are preferably each independently selected from sulpho, carboxy, phosphato, hydroxy and amino.

In view of the foregoing preferences, a preferred compound of Formula (1) is of Formula (2):



Formula (2)

wherein:

- each MPc independently is a copper or nickel phthalocyanine;
- R^2 and R^3 are each independently H or optionally substituted alkyl;
- each m independently is 1 to 4; and
- each n independently has a value of 1 to 4;

provided that at most one of the groups represented by MPc carries a substituent of formula $-\text{SO}_2\text{NH}_2$.

Preferably the value of the value of $(m + n)$ on the MPc group carrying the sulpho and sulphonamide substituents is from 2 to 6, more preferably 3 to 4.

Preferably the compounds described hereinbefore are water-soluble.

According to a second aspect of the present invention there is provided a composition comprising a compound of Formula (1) and a liquid medium.

Preferred compositions comprise:

- (a) from 0.01 to 30 parts of a compound of Formula (1), more preferably Formula (2); and
 - (b) from 70 to 99.99 parts of a liquid medium;
- wherein all parts are by weight and the number of parts of $(a)+(b)=100$.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare more dilute inks and also reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially pentane-1,5-diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Although not usually necessary, further colorants may be added to the liquid medium to modify the shade and performance properties of the composition. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International. Addition of such further dyes can increase overall solubility leading to less clogging (nozzle blockage) for the resultant ink.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50° to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferably the composition has been filtered through a filter having a mean pore size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter which could otherwise block the fine nozzles found in many ink-jet printers.

The composition preferably has a total concentration of divalent and trivalent metal ions (other than those bound to the nitrogen atoms at the phthalocyanine nucleus) of below 1000, more preferably below 100, especially below 20, more especially below 10 parts per million by weight relative to the total weight of the composition. Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

The liquid medium may also of course contain further components which are conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

The composition may be an ink, especially an ink-jet printing ink, or a liquid dye concentrate which is used to prepare inks. The concentrates are useful as a means for

transporting colorant and so minimising costs associated with drying the dye and transporting excess liquid.

The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular the compounds of Formula (1) are stable to oxidative gases such as ozone, nitrous oxide, NO and NO₂. The compounds of Formula (1) particularly benefit from their stability to ozone.

A third aspect of the invention provides a process for printing an image on a substrate comprising applying a composition according to the second aspect of the current invention to a substrate by means of an ink-jet printer.

The ink-jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the orifice, thereby causing the composition to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the composition from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character.

A fourth aspect of the present invention provides a substrate, especially a paper, an overhead projector slide, a textile material, a plastic, glass and metal printed with a composition, a compound or by means of a process as hereinbefore described.

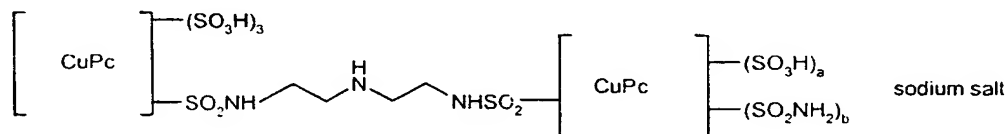
A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described according to the second aspect of the present invention.

A sixth aspect of the invention is a method for the coloration of a substrate which comprises applying thereto a compound of Formula (1).

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

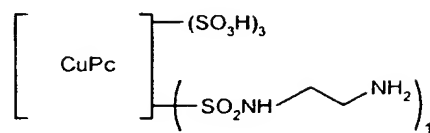
Preparation of:



wherein a and b are > 0 and (a + b) is 3.

Step 1

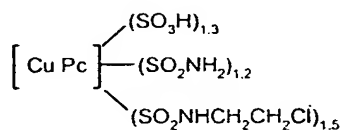
Preparation of:



Sulphuric acid (9.4g) was added to chlorosulphonic acid (192g) followed by copper phthalocyanine (38.4g) below 60°C. The reaction mixture was heated at 130-140°C for 2hr, cooled and drowned out into ice/water (480g). The precipitate was filtered, washed with 0.5M HCl (600ml) and added stepwise to a stirred solution of ethylene diamine (4g) in ice/water (340g). This reaction mixture was heated to 40°C at pH 7-8 for 2hr, cooled and the pH lowered to pH 3-4 using concentrated HCl. The precipitate was filtered and washed with saturated brine to give the intermediate shown above.

Step 2

The intermediate from Step 1 (23 g) was added stepwise to a stirred solution of C.I. Reactive Blue 23 (31.9g) in water (800ml) at room temperature and pH 9-10.



C.I. Reactive Blue 23

The reaction mixture was heated at 70°C for 4.5 hr at pH 9-10 then cooled and the pH lowered to pH 3-4 with concentrated HCl. The precipitated solid was filtered-off, washed with 0.5M HCl, converted to the sodium salt, desalinated and dried to give the product (44.6g) having absorbance maxima at 620 and 665 nm. Analysis by mass spectroscopy revealed multiple products of which the title product was the major component

Example 2

Preparation of inks

Inks were prepared by dissolving 3 parts (by weight) of the dye in a stock solution of 5 parts 2-pyrrolidone, 5 parts thiodiglycol, 2 parts Surfynol 465 (a surfactant commercially available from Air Products Inc.) and 85 parts distilled water, adjusted to pH 8.5 to 9 using sodium hydroxide. The resultant inks were as follows:

Ink (1) contained Dye (1)

Comparative Ink contained the Comparative Dye

The comparative dye was C.I. Direct Blue 199, a copper phthalocyanine dye obtained from Avecia Limited.

Each ink was filtered through a 0.45µm filter and put into one chamber of a Canon trichamber inkjet cartridge.

"Surfynol" is a registered trade mark of Air Products Inc.

Ink-jet Printing

Ink 1 was ink-jet printed onto each of the substrates shown in Table A and Table B using a Canon 4300 IJ printer, the following results were obtained:

The CIE colour co-ordinates of each print (a, b, L, Chroma and hue) were measured using a Xrite 983 Spectrodensitometer with 0°/45° measuring geometry with a spectral range of 400-700nm at 20nm spectral intervals, using illuminant C with a 2° (CIE 1931) observer angle and a density operation of status T. No less than 4 measurements were taken diagonally across a solid colour block on the print with a size greater than 10mm x 10mm.

The OD is the optical density of the printed paper, as measured by the Xrite 983 Spectrodensitometer.

Table A: Ink 1

| Substrate | OD | L | a | b | Hue | Chroma |
|---|-------|----|-----|-----|-----|--------|
| Canon HG201 - High Gloss Film | 2.279 | 54 | -34 | -45 | 233 | 56 |
| SEC Photopaper | 1.926 | 49 | -20 | -51 | 249 | 55 |
| SEC Coated 720dpi Photo quality Ink-jet paper | 1.181 | 58 | -27 | -33 | 230 | 43 |
| Xerox 4024 | 0.997 | 60 | -21 | -35 | 240 | 41 |

Ozone Fastness

Ink 1 and the comparative ink were printed onto Canon HG201 High Gloss Film using a Canon 4300 IJ printer. The printed substrate was then assessed for ozone stability using an ozone test cabinet from Hampden Test Equipment. The test was carried out for two and a half hours at 40°C and 55% relative humidity in the presence of 400 parts per hundred million of ozone. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone using an Xrite 983 Spectrodensitometer. Thus, the lower the %OD loss the greater the ozone fastness.

Results are shown below in Table C and these clearly demonstrate the advantage of inks based on dyes of this invention over the comparative dye based ink.

Table B

| Ink | Ozone Fastness %OD Loss |
|-----------------|-------------------------|
| Ink 1 | 5.3% |
| Comparative Ink | 29.2% |

Further Inks

The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the Dye made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE I

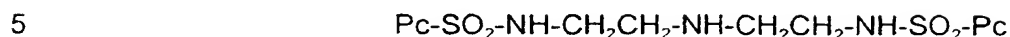
| Example | Dye Content | Water | PG | DEG | NMP | DMK | NaOH | Na Stearate | IPA | MEOH | 2P | MIBK |
|---------|-------------|-------|----|-----|-----|-----|------|-------------|-----|------|----|------|
| 1 | 2.0 | 80 | 5 | | 6 | 4 | | | | | 5 | |
| 1 | 3.0 | 90 | | 5 | 5 | | 0.2 | | | 5 | 1 | |
| 1 | 10.0 | 85 | 3 | | 3 | | | | | | | 1 |
| 1 | 2.1 | 91 | | 8 | | | | | 4 | | | 5 |
| 1 | 3.1 | 86 | 5 | | | | 0.5 | 0.2 | | | 9 | |
| 1 | 1.1 | 81 | | | 9 | | | 0.5 | 6 | 10 | 5 | 4 |
| 1 | 2.5 | 60 | 4 | 15 | 3 | 3 | | | 10 | | | |
| 1 | 5 | 65 | | 20 | | 5 | | | | 6 | | 5 |
| 1 | 2.4 | 75 | 5 | 4 | | | | | | | | |
| 1 | 4.1 | 80 | 3 | 5 | 2 | 10 | | 0.3 | 5 | 4 | 6 | 5 |
| 1 | 3.2 | 65 | | 5 | 4 | 6 | | | | 4 | | |
| 1 | 5.1 | 96 | | | | | | | 5 | | | |
| 1 | 10.8 | 90 | 5 | | | | | | | | | |
| 1 | 10.0 | 80 | 2 | 6 | 2 | 5 | | | 1 | | 4 | |
| 1 | 1.8 | 80 | | 5 | | | | | | | 15 | |
| 1 | 2.6 | 84 | | | 11 | | | | | | 5 | |
| 1 | 3.3 | 80 | 2 | | | 10 | | | 3 | 2 | | 6 |
| 1 | 12.0 | 90 | | | | 7 | 0.3 | | | | | |
| 1 | 5.4 | 69 | 2 | 20 | 2 | 1 | | | | | 3 | 3 |
| 1 | 6.0 | 91 | | | 4 | | | | | | 5 | |

TABLE II

| Example | Dye Content | Water | PG | DEG | NMP | CET | TBT | TDG | BDL | PHO | 2P | PI2 |
|---------|-------------|-------|----|-----|-----|------|-----|-----|-----|------|----|-----|
| 1 | 3.0 | 80 | 15 | | | 0.2 | | | | | 5 | |
| 1 | 9.0 | 90 | | 5 | | | | | | 1.2 | | 5 |
| 1 | 1.5 | 85 | 5 | 5 | | 0.15 | 5.0 | 0.2 | | 0.12 | | |
| 1 | 2.5 | 90 | | 6 | 4 | | | | | | | |
| 1 | 3.1 | 82 | 4 | 8 | | 0.3 | | | 5 | 0.2 | | 6 |
| 1 | 0.9 | 85 | | 10 | | | | | | | | |
| 1 | 8.0 | 90 | | 5 | 5 | | | 0.3 | | | | |
| 1 | 4.0 | 70 | | 10 | 4 | | | | 1 | | 4 | 11 |
| 1 | 2.2 | 75 | 4 | 10 | 3 | | | | 2 | | 6 | |
| 1 | 10.0 | 91 | | | 6 | | | | | | 3 | |
| 1 | 9.0 | 76 | | 9 | 7 | | 3.0 | | | 0.95 | 5 | |
| 1 | 5.0 | 78 | 5 | 11 | | | | | | | 6 | |
| 1 | 5.4 | 86 | | | 7 | | | | | | 7 | |
| 1 | 2.1 | 70 | 5 | 5 | 5 | 0.1 | 0.2 | 0.1 | 5 | 0.1 | 5 | |
| 1 | 2.0 | 90 | | 10 | | | | | | | | |
| 1 | 2 | 88 | | | | | | 10 | | | | |
| 1 | 5 | 78 | | | 5 | | | 12 | | | 5 | |
| 1 | 8 | 70 | 2 | | 8 | | | 15 | | | 5 | |
| 1 | 10 | 80 | | | | | | 8 | | | 12 | |
| 1 | 10 | 80 | | 10 | | | | | | | | |

CLAIMS

1. A compound of Formula (1):



Formula (1)

10 wherein each Pc is independently an optionally substituted phthalocyanine group provided that at most one of the groups represented by Pc carries a substituent of formula $\text{-SO}_2\text{NH}_2$.

15 2. A compound according to claim 1 wherein the phthalocyanine groups are each independently selected from metal-free phthalocyanines and metal containing phthalocyanines.

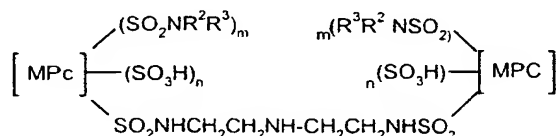
20 3. A compound according to any one of the preceding claims wherein the phthalocyanine groups are each independently selected from copper phthalocyanine and nickel phthalocyanine.

4. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulpho substituent.

25 5. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulphonamide substituent of the formula $\text{SO}_2\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are each independently H or optionally substituted alkyl.

30 6. A compound according to any one of the preceding claims wherein at least one of the phthalocyanine groups carries a sulpho substituent and a sulphonamide substituent of the formula $\text{SO}_2\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are each independently H or optionally substituted alkyl.

7. A compound according to any one of the preceding claims of Formula (2):



Formula (2)

wherein:

- each MPc independently is a copper or nickel phthalocyanine;
R² and R³ are each independently H or optionally substituted alkyl;
each m independently is 1 to 4; and
each n independently has a value of 1 to 4;

provided that at most one of the groups represented by Pc carries a substituent of formula -SO₂NH₂.

8. A compound according to any one of the preceding claims which is water-soluble.

9. A composition comprising a compound according to any one of claims 1 to 8 and a liquid medium.

10. A composition according to claim 9 which is an ink or liquid dye concentrate.

11. A process for printing an image on a substrate comprising applying a composition according to claim 9 to a substrate by means of an ink-jet printer.

12. A paper, an overhead projector slide, a textile material, a plastic, glass and metal printed with a composition according to claim 9, with a compound according to any one of claims 1 to 8 or by means of a process according to claim 11.

13. An ink-jet printer cartridge comprising a chamber and a composition wherein the composition is in the chamber and the composition is as described in claim 9.

14. A method for the coloration of a substrate which comprises applying thereto a compound according to any one of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00565

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09B47/26 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| Y | US 3 674 783 A (TOBEL HANS VON) 4 July 1972 (1972-07-04) abstract; examples 3,4,31 --- | 1-14 |
| Y | EP 0 418 792 A (CANON KK) 27 March 1991 (1991-03-27) the whole document --- | 1-14 |
| Y | WO 98 49240 A (CARR KATHRYN ; ZENECA LTD (GB)) 5 November 1998 (1998-11-05) the whole document --- | 1-14 |
| Y | WO 97 13812 A (KENYON RONALD WYNFORD ; ZENECA LTD (GB); MISTRY PRAHALAD MANIBHAI () 17 April 1997 (1997-04-17) the whole document --- | 1-14 |
| | -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

27 April 2001

Date of mailing of the international search report

25/05/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Dauksch, H

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/GB 01/00565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | CHEMICAL ABSTRACTS, vol. 69, no. 16, 14 October 1968 (1968-10-14) Columbus, Ohio, US; abstract no. 60042z, XP002166210 abstract & CZ 121 235 A (CHMATAL VLADIMIR ET AL) 15 December 1966 (1966-12-15) | 1-9 |
| A | US 3 325 511 A (T. E. LESSLIE, W.J. BRYAN) 13 June 1967 (1967-06-13) column 2, line 45 - last line; examples 19-34 | 1 |
| A | FR 2 643 379 A (SANDOZ SA) 24 August 1990 (1990-08-24) the whole document | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/00565

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|
| US 3674783 | A | 04-07-1972 | NONE | |
| EP 0418792 | A | 27-03-1991 | JP 2942319 B JP 3185080 A AT 125854 T DE 69021306 D DE 69021306 T US 5123960 A | 30-08-1999 13-08-1991 15-08-1995 07-09-1995 25-01-1996 23-06-1992 |
| WO 9849240 | A | 05-11-1998 | AU 6928498 A EP 0975698 A | 24-11-1998 02-02-2000 |
| WO 9713812 | A | 17-04-1997 | AU 6993696 A GB 2320252 A,B JP 11515048 T US 5922116 A | 30-04-1997 17-06-1998 21-12-1999 13-07-1999 |
| CZ 121235 | A | | NONE | |
| US 3325511 | A | 13-06-1967 | NONE | |
| FR 2643379 | A | 24-08-1990 | CH 679308 A DE 4005015 A GB 2228737 A,B IT 1240772 B JP 2261865 A JP 2873305 B SE 465463 B SE 9002279 A US 5084068 A | 31-01-1992 30-08-1990 05-09-1990 17-12-1993 24-10-1990 24-03-1999 16-09-1991 16-09-1991 28-01-1992 |